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SPRING COLLEGE IN MATERIALS SCIENCE ON
"NUCLEATION, GROWTH AND SEGREGATION IN MATERIALS
SCIENCE AND ENGINEERING"
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TRANSPORT PROCESSES
(INCLUDING RADIATION ENHANCED DIFFUSION)
Part I

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Overview of Lectures

1) Description of diffusion on various levels and basic diffusion mechanisms in solids

2) Radiation-induced and radiation-enhanced diffusion, and related phenomena

3) Diffusion in the elemental semiconductors Si and Ge

4) Diffusion in disordered media (amorphous metallic alloys)

5) Self-organization in solids by anisotropic transport of matter

Description of Diffusion on Various

Level

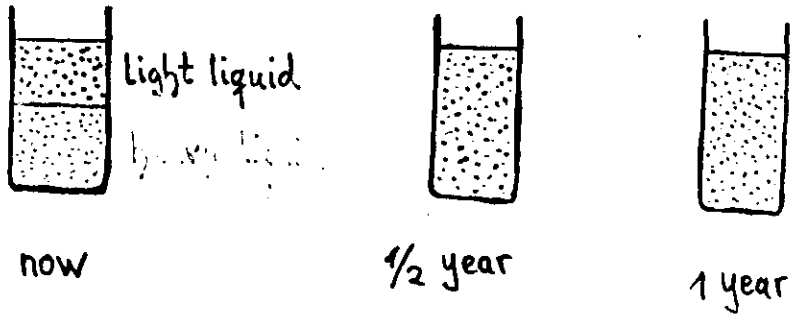
and

Basic Diffusion Mechanisms in Solids

DIFFUSION IN SOLIDS

Theory & Experiments

What is diffusion ?



Phenomenological description

$$\vec{j} = -D \, \mathrm{grad}\, C \qquad (1)$$

Fick's 1st Law

D = diffusion coefficient $\left[\frac{m^2}{s}\right]$

- Onsager's linear irreversible thermodynamics : first-order Kinetic coefficient
- tensor of rank 2 (anisotropic diffusion)
- isotropic media or cubic crystals : D = scalar

Conservation of diffusing particles (exclusion of particle reactions):

$$-\partial C/\partial t = \operatorname{div} \vec{j} \qquad (2)$$

Continuity Equation

1) + (2): $$\boxed{\partial C/\partial t = \operatorname{div}(D \operatorname{grad} C)} \qquad (3a)$$

Fick's 2nd Law (most general form)

Annotation: $D \neq D(t)$ $\left[D \neq D(C(t))\right]$

$$\partial C/\partial t = D \Delta C \qquad (3b)$$

Fick's 2nd Law (most popular form)

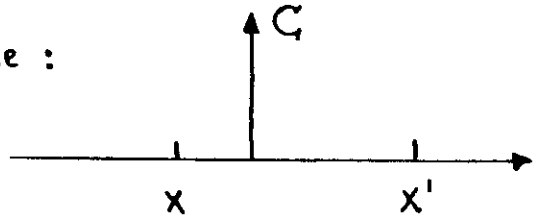
1-dimensional case: $$\boxed{\partial C/\partial t = D\, \partial^2 C/\partial x^2}$$

heat conduction eq.: $\partial T/\partial t = \varkappa\, \partial^2 T/\partial x^2$

Schrödinger eq.: $\partial \Psi/\partial t = (i\hbar/2m)\, \partial^2 \Psi/\partial x^2$

classical wave eq.: $\partial^2 W/\partial t^2 = c^2\, \partial^2 W/\partial x^2$

1-dim. case:



Random walk:

$P_t(x,x')$ = probability that a particle has migrated from $x \to x'$ during t

$$\boxed{C(x',t) = \int_{x=-\infty}^{+\infty} C(x,0) \cdot P_t(x,x')\, dx} \qquad (4)$$

Annotation:

1) spatial homogeneity: $P_t = P_t(X)$, $X = x - x'$

2) isotropy: $P_t(X) = P_t(-X)$

$$\boxed{C(x',t) = \int_{X=-\infty}^{+\infty} C(x'+X, 0)\, P_t(X)\, dX} \qquad (5)$$

Fokker–Planck Equation

Expansion in power series of t and X:

Note: $\int_{-\infty}^{+\infty} P_t(X)\,dX = 1$ (normalization)

$\int_{-\infty}^{+\infty} X\,P_t(X)\,dX = 0$

$\int_{-\infty}^{+\infty} X^2\,P_t(X)\,dX \equiv \overline{X^2} \neq 0$

$\lim_{t\to 0} P_t(X) \neq 0$ only for small X

$$\partial C/\partial t + \ldots = \frac{\overline{X^2}}{2t}\,\partial^2 C/\partial x^2 + \ldots \quad (6$$

Comparison with Fick's 2nd Law:

$$D \equiv \frac{\overline{X^2}}{2t} \quad (7a)$$

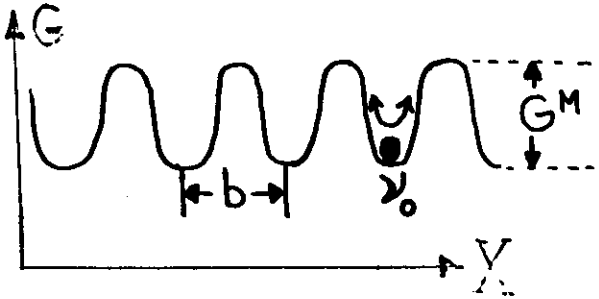
$$\overline{X} \simeq \sqrt{\overline{X^2}} = \sqrt{2Dt} \quad (7b)$$

mean diffusion length

Atomistic Description

Specialization:
- crystalline solids
- thermally activated diffusic

$p, T = \text{const}$:



G^M = Gibbs free energy of migration

Jump frequency: $\nu = \nu_0 \exp(-G^M/kT)$

$G = H - TS$

$$\nu = \nu_0 \exp\left(\frac{S^M}{k}\right)\exp(-H^M/kT) \quad (8$$

ν_0^*

Diffusion coefficient:

$D = \overline{X^2}/2t$

$1/t \propto \nu$

$\overline{X^2} = b^2 \propto a^2$

$$D^{(X)} = g\,a^2\,\nu = g\,a^2\,\nu_0^*\exp(-H^M/kT) \quad (1$$

Direct vs. Indirect Diffusion

Direct diffusion (see above)

The diffusing particles perform random walks.

The diffusing particles are mobile per se, i.e., diffusion vehicles are not involved.

Indirect diffusion

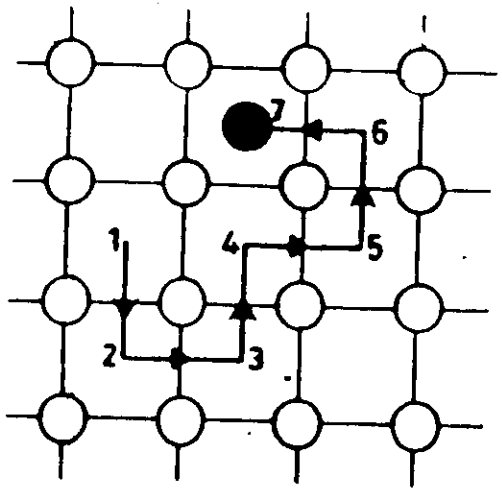
Without the aid of diffusion vehicles the particles under consideration cannot move.

It is the diffusion vehicles which perform random walks.

The particles considered undergo a non-random, correlated diffusion as a result of the diffusion of the vehicles

Direct Diffusion

Most prominent mechanism:



direct interstitial mechanism

Characteristic feature:

low migration enthalpy ($H^M \lesssim 1eV$)

Examples:

Fe, Cu, Li, Pd (see below) in Si

C, N in α-Fe

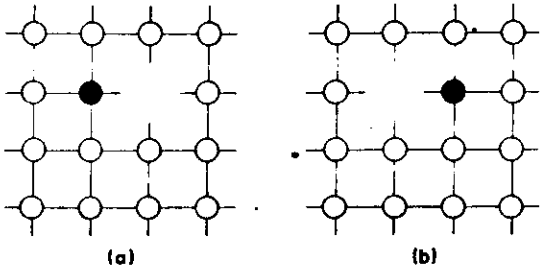
O in Ta

Indirect Diffusion

Most elementary mechanisms involve

vacancies or self-interstitials

1) Vacancy mechanism



Examples:

self-diffusion in metals

diffusion of substitutional solutes in metals

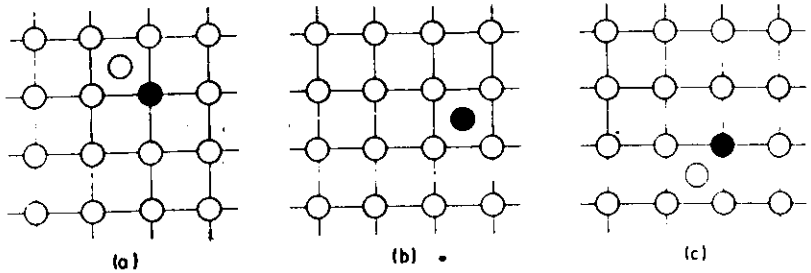
self-diffusion in Ge

diffusion of substitutional Group-III and Group-V dopants in Ge

fat Group-V dopants (e.g. As, Sb) in Si

2) Indirect interstitial mechanism

(interstitialcy mechanism)



Examples:

self-diffusion in Si (above 1000°C)

small Group-III dopants (e.g., B) in Si

self-diffusion in ice (above −50°C)

Why is the vacancy mechanism widely known in contrast to the interstitialcy mechanism?

Diffusion Coefficients

Direct diffusion (see above [Eq.(9)]):

$$D = \underbrace{g a^2 \nu_0^*}_{D_0} \exp\left(-H^M/kT\right)$$

Indirect diffusion

Corresponding expression for the diffusion coefficient of the diffusion vehicles:

$$D_v = D_{v,0} \exp\left(-H_v^M/kT\right) \quad [v = V, I] \qquad (10)$$

Diffusion coefficient of the particle diffusing via V or I:

$$D_v^S = f_v C_v D_v \qquad (11)$$

$$0 \le f_v \le 1 \qquad (12)$$

f_v: correlation factor (see below)

self-diffusion coefficient

or

diffusion coefficient of substitutional solutes

Thermal Equilibrium: $C_v = C_v^{eq} \equiv \exp\left(-G_v^F/kT\right)$

(10) + (13) in (11):

$$D_v^S = D_{v,0}^S \exp\left[-\left(H_v^F + H_v^M\right)/kT\right] \qquad (14)$$

final expression for coefficient of indirect diffusion

Characteristic feature:

high self-diffusion enthalpy $\left(H_v^F + H_v^M \gtrsim 2\,eV\right)$

General case of indirect diffusion (superposition of vacancy mechanism and interstitialcy mechanism)

$$D^S = D_V^S + D_I^S \qquad (15)$$

Note: Comparable significance of both contributions is restricted to a small temperature regime

Examples:
- self-diffusion in Si at about 1000 °C
- self-diffusion in ice at about −50 °C
- Group-III and Group-V elements in Si (> 1000 °C: fat Group-V dopants [e.g., Sb] prefer V mechanism,

Correlation Factor

$$D_v^s = f_v C_v D_v \qquad (11)$$

$$D_v^s = D_{v,0}^s \exp\left[-\left(H_v^F + H_v^M\right)/kT\right] \qquad (14)$$

$$D_{v,0}^s \sim f_v$$

Demonstration for V mechanism

3d or 2d case:

random walk of V
correlated walk of diffusing atom
⟶ high probability that preceding jump is cancelled
⟶ $f_V < 1$

linear chain: o o o □ o ● o o o
⟶ $f_V = 0$

direct diffusion: $D^s = D \ldots C = 1 \; f = 1$

Rate Equations

Violation of conservation of particles due to reactions:

$$\frac{\partial c}{\partial t} = D\,\Delta c + \left(\frac{\partial C}{\partial t}\right)_{\text{reaction}} \qquad (16)$$

Usually mathematical treatment is difficult!

Alternative: Rate-Equation Treatment

Restriction to spatially averaged concentrations c (atomic fractions)

First-Order Reaction

Example: Supersaturation c_V of quenched-in vacancies anneals out by vacancy migration to a fixed concentration c_S of unsaturable sinks:

(mobile) V + (immobile) S
⟶ (immobile) S

$$\underbrace{-\frac{dc_V}{c_V(t)\,dt}}_{\text{probability that a vacancy disappears during unit time}} = \frac{\nu_V}{\Lambda_V} \qquad (17)$$

ν_V = average number of jumps per unit time

Λ_V = average number of jumps required to reach a sink

$$\Lambda_V = \alpha / C_S . \qquad (18)$$

(18) in (17):

$$\frac{dc_V}{dt} = -\frac{C_S\, c_V^1(t)}{\alpha}\, \underbrace{\nu_{V,0}^*\, \exp\left(-H_V^M / kT\right)}_{\nu_V} \qquad (19)$$

Second-Order (Bimolecular) Reaction

Example: Supersaturations of radiation-induced vacancies and self-interstitials anneal out by mutual annihilation:

$$(\text{mobile})\ I + (\text{immobile})\ V \longrightarrow 0$$

$$-\frac{dc_I}{c_I(t)\,dt} = \frac{\nu_I}{\Lambda_I} \qquad (20)$$

$$\Lambda_I(t) = \beta / c_V(t) \qquad (21)$$

$$c_V(t) = c_I(t) \qquad (22)$$

(21) & (22) in (20):

$$\frac{dc_I}{dt} = -\frac{c_I^2(t)}{\beta}\, \nu_{I,0}^*\, \exp\left(-H_I^M / kT\right) \qquad (23)$$

More general (but not most general) form of rate equations:

$$\frac{dc}{dt} = -F(c)\, \exp\left(-H^M / kT\right) \qquad (24)$$

Removable restrictions:

One mobile species undergoes one reaction

Inherent deficiency:

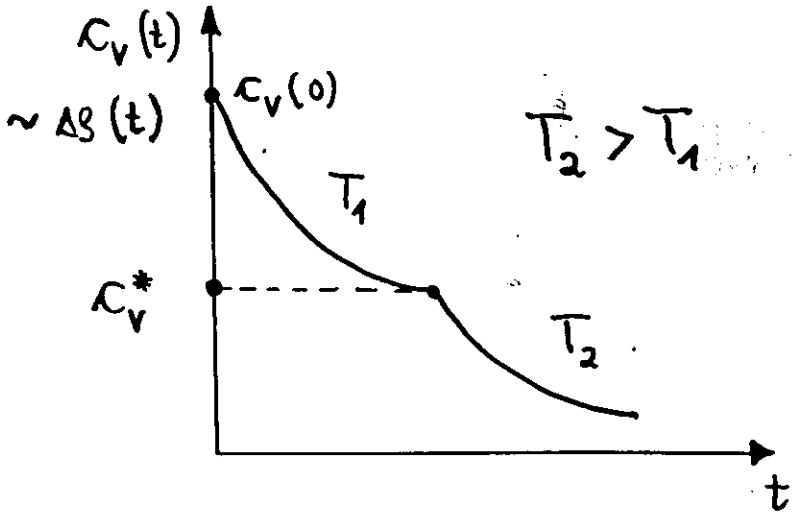
A Rate-Equation Application

Self-diffusion in metals via vacancies:

$$D_V^{SD} = D_{V,0}^{SD} \exp\left[-\underbrace{\left(H_V^F + H_V^M\right)}_{H^{SD}}/kT\right] \quad (25)$$

Problem: Splitting up of H^{SD} in H_V^F and H_V^M

One possibility: Determination of H_V^M from the annealing out of quenched-in vacancies by the **change-of-slope** method:



$$\left(dc_V/dt\right)_{T_1} = -F(c_V^*)\exp\left(-H_V^M/kT_1\right) \quad (26a)$$

$$\left(dc_V/dt\right)_{T} = -F(c_V^*)\exp\left(-H_V^M/kT_2\right) \quad (26b)$$

(26a) : (26b)

$$\rightarrow \quad H_V^M = -k\,\frac{T_1 T_2}{T_2 - T_1}\,\ln\left[\frac{\left(\frac{dc_V}{dt}\right)_{T_1}}{\left(\frac{dc_V}{dt}\right)_{T_2}}\right] \quad (\ldots$$

$$H_V^F = H^{SD} - H_V^M$$

Summary:

a) Phenomenological description of diffusion

b) Statistical description of diffusion

c) Atomistic description of thermally activated diffusion in solids

d) Basic diffusion mechanisms in solids

e) Rate-equation treatment of diffusion-controlled reactions in solids, including an application